Electron density distribution of bilayer nanographene and band structures of boron-carbon-nitride systems

Kikuo Harigaya and Hiroshi Imamura

Nanosystem Research Institute, AIST, Tsukuba 305-8568, Japan

Abstract

Bilayer graphene nanoribbon with zigzag edge is investigated with the tight binding model. Two stacking structures, α and β, are considered. The band splitting is seen in the α structure, while the splitting in the wave number direction is found in the β structure. The local density of states in the β structure tend to avoid sites where interlayer hopping interactions are present. The calculation is extended to the boron-carbon-nitride systems. The qualitative properties persist when zigzag edge atoms are replaced with borons and nitrogens.

Keywords: A. Nanostructures, D. Electronic structure, D. Surface properties

1. Introduction

The graphite, multi-layer, and single-layer graphene materials have been studied intensively, since the electric field effect has been found in atomically thin graphene films [1]. These materials can be regarded as bulk systems. On the other hand, nanographenes with controlled edge structures have been predicted to have localized states along the zigzag edges [2]. The presence of the edge states has been observed by experiments of scanning tunneling spectroscopy [3,4]. Thus, the studies of the edge states are one of the interesting topic of the field. The recent atomic bottom-up fabrication of nanoribbons really promotes experimental and theoretical investigations [5].

In the previous paper [6], the tight binding model has been solved numerically, and effects of interlayer interactions have been considered. In the β structure [Fig. 1 (b)], the split of the energy bands is not seen compared with that of the α structure [Fig. 1 (a)]. The difference of the band split in the α and β structures appears. Number of states in the energy window for the positive wave number has been calculated for the single layer, α, and β structures. The dependence of the energy reflects the band structures, and this will appear in quantization of conductance experimentally.

In this paper, we will report the electron density distribution in nanographene materials with zigzag edges including the inter-layer interactions. The calculation is extended to the boron-carbon-nitride systems, too. We report the band structures of the single and bilayer systems.

2. Model

The following tight binding model is used in the calculation:

$$\begin{aligned} H = & -t \sum_{\langle i,j\rangle,\sigma} (c^{\dagger}_{i,\sigma} c_{j,\sigma} + \text{h.c.}) \\ & -t \sum_{\langle i,j\rangle,\sigma} (d^{\dagger}_{i,\sigma} d_{j,\sigma} + \text{h.c.}) \\ & -t_1 \sum_{\langle i,j\rangle,\sigma} (c^{\dagger}_{i,\sigma} d_{j,\sigma} + \text{h.c.}), \end{aligned} \tag{1}$$

where $c_{i,\sigma}$ and $d_{i,\sigma}$ are the annihilation operators of electrons at the lattice site i of the spin σ on the upper and lower layers, respectively. The quantity t is the hopping integral of π electrons between neighboring lattice sites. Two stacking patterns, shown in Figs. 1 (a) and (b), are considered. They are named as α and β structures, respectively. This convention has been used in the literature [7]. There are $N_z = 10$ zigzag lines in upper and lower layers. Inclusion of the bond alternations [8,9] would be interesting, but it is not treated in this paper.

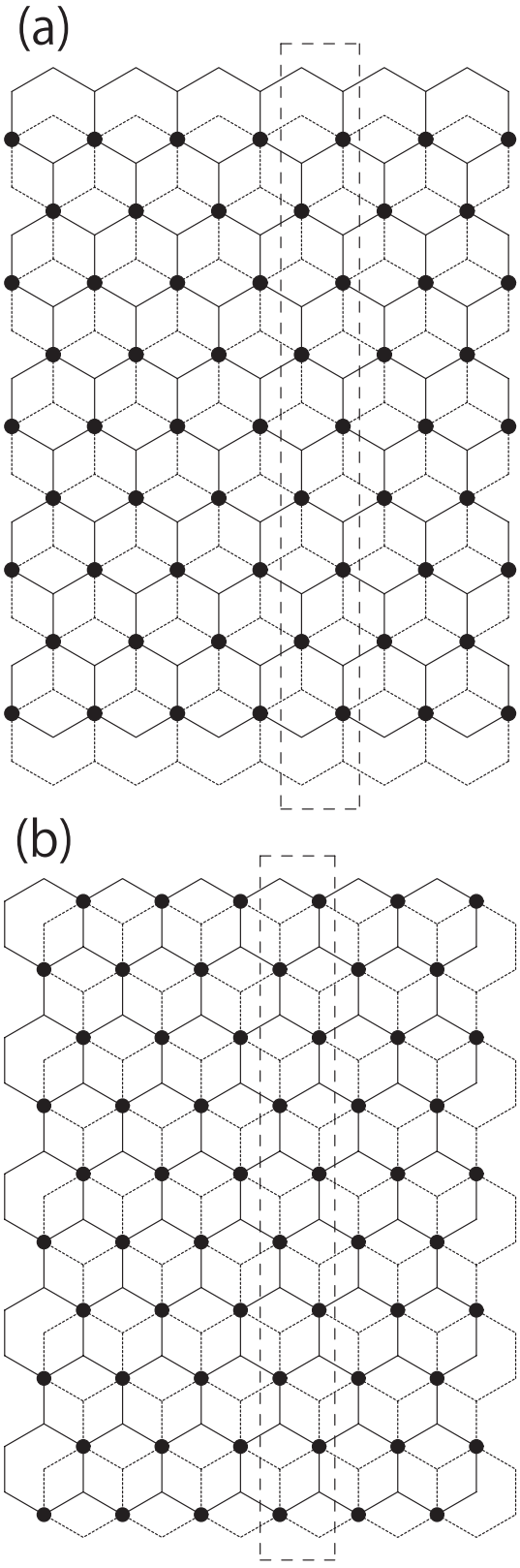
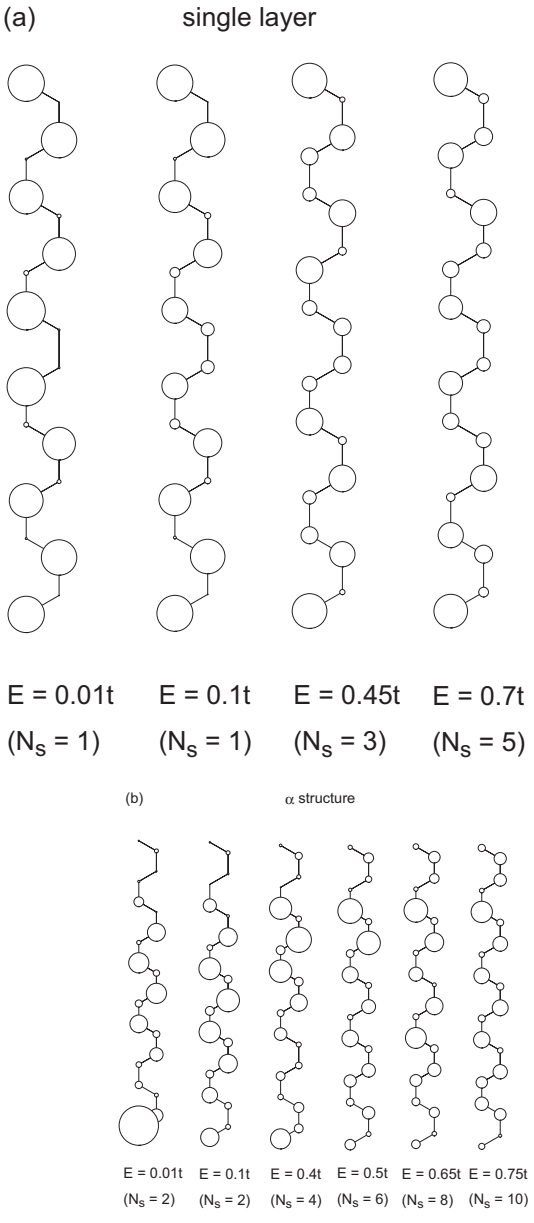


Fig. 1. A-B stacked bilayer graphene nanoribbon with zigzag edges. The upper layer is shown by the solid lines, and the lower layer by dotted lines. In the α structure (a), the upper layer is shift by the bond length downward to the position of the lower layer. The region surrounded by the dashed line is the unit cell in the direction of the one dimensional direction. At the circles, two carbon atoms of the upper and lower layers overlap completely, and there is the weak hopping interaction t_1 here. In (b), the β structure is shown, where the lower layer is shift to the right-down direction so the stacking pattern is different from that of the α structure. The convention of the α and β structures is the same used in the paper [7]. In the area surrounded by the dashed lines, the unit cell is displayed.

3. Electron density in the real space

In order to understand effects of the band split clearly, it is useful to watch the distribution of electron density in the real space. Here, we calculate electron density by changing the energy window. Figure 2 shows local density of states of electrons in the unit cell of the upper layer. The energy is shown below each figure, with the number of states N_s crossing at the energy for the region of positive wave number. The diameter of the circle is proportional to the electron density. The total electron number in the unit cell is normalized to be constant divided by N_s, in order to eliminate the effects of enlargement of circles due to large degeneracy. In Fig. 2, the electron density is displayed for $N_z = 10$, so there are 20 atoms in the unit cell. In the single layer (a), the electron density is symmetric with respect to the center of the unit cell. At the energy $E = 0.01t$, the electron density is large at A type sites in the upper part, while it is large at B type sites in the lower part. There will be an edge state at $E = 0$, but the electron density has already intrude into the inner part at this energy. As the energy increases from $E = 0.1t$ to $0.7t$, the electron density moves gradually from A type to B type sites (or, from B type to A type sites). After interlayer interaction $t_1 = 0.1t$ is taken into account, the spatial symmetry is lost as shown for the α (b) and β (c) structures. The energy is changed from $E = 0.01t$ to $0.75t$ in (b), and from $E = 0.01t$ to $0.7t$ in (c). N_s is increased by steps of jumps. Both in (b) and (c), the electron density is relatively larger at odd number sites from the top of the unit cell. It is smaller at even number sites in the inner part. The result looks similar at a glance. However, there is a difference. The interlayer interaction t_1 is present at odd number sites of the unit cell in the upper layer in Fig 1. (a). So, this interaction gives rise bonding anti-bonding split of energy band. The electrons favor to have large

amplitudes at odd number sites in the inner part. On the other hand, the interaction t_1 is located at even number sites in Fig. 1 (b). The electrons tend to avoid the interaction t_1, and the removal of the degeneracy occurs in the direction of the wave number. In this way, the electron density in the real space is related mutually with the difference in changes, seen in the band structures of the bilayer nanoribbons. These findings will be observed possibly by conduction and STM experiments.



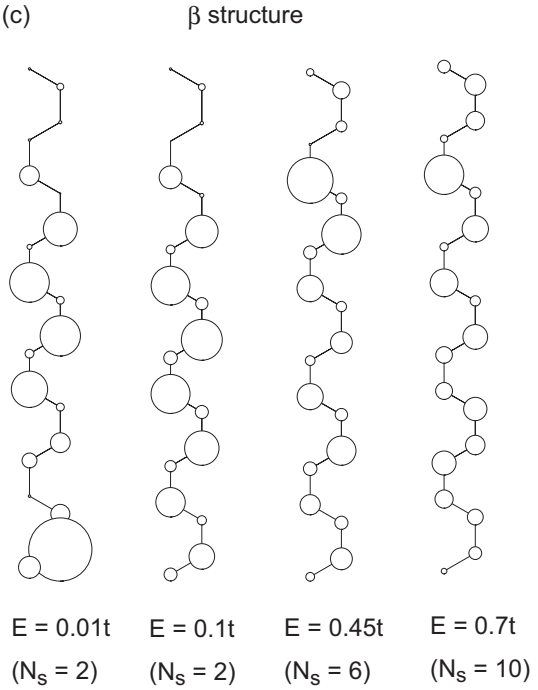


Fig. 2. Local density of states in the unit cell of the upper layer for the single layer (a), α structure (b), and β structure (c). The density is proportional to the diameter of the circle. The energy is shown below each figure, with the number of states N_s crossing at the energy for the region of positive wave number.

4. Band structures of the BCN systems

The calculation is extended to the boron-carbon-nitride (BCN) systems [10]. The stacking patterns are considered with the spatial inversion symmetry. The presence of B and N atoms is taken into account by the site energies $E_B = +t$ and $E_N = -t$, as has been used in the paper [11].

Energy band structures of the $N_z = 10$ systems are displayed in Fig. 3, for the single layer (a), α structure (b), and β structure (c). The interlayer interaction strength is $t_1 = 0.1t$. In (b), the split of the energy bands is seen compared with Fig. (a). In contrast, split in the perpendicular direction is small in Fig. (c), except for the lowest unoccupied state and highest occupied state, which have large amplitude near edge atoms. In order to see split structures clearly, details near the Brillouin zone edge are magnified for the single layer (d), α structure (e), and β structure (f). In (e) and (f), the energy bands of the single layer are shown by the red lines for

comparison. We find that the qualitative properties between the difference of the energy band splits of the α and β structures persist when zigzag edge atoms are replaced with borons and nitrogens. This property is confirmed by looking at the numerical data, also.

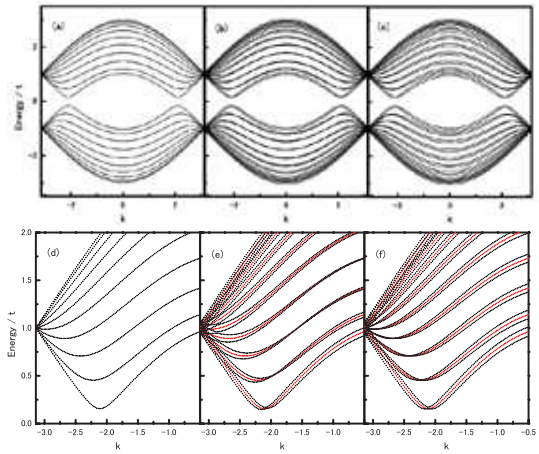


Fig. 3. Energy band structures of the boron-carbon-nitride nanoribbons for the single layer (a), α structure (b), and β structure (c). Details near the Brillouin zone edge are magnified for the single layer (d), α structure (e), and β structure (f). In (e) and (f), the energy bands of the single layer are shown by the red lines for comparison.

5. Summary

In summary, weak interlayer interactions have been considered for the bilayer graphene nanoribbon with zigzag edge. The α and β stacking structures have been considered. The band splitting is seen in the α structure, while the splitting in the wave number direction is found in the β structure [6]. The local density of states in the β structure tend to avoid sites where interlayer hopping interactions exist. The calculation has been extended to the boron-carbon-nitride systems. The qualitative properties persist when zigzag edge atoms are replaced with borons and nitrogens.

Acknowledgemwnts

This research was supported by the International Joint Work Program of Daeduck Innopolis under the Ministry of Knowledge Economic (MKE) of the Korean Government.

References

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science **306**, 666 (2004).

[2] M. Fujita, K. Wakabayashi, K. Nakada, and K. Kusakabe, J. Phys. Soc. Jpn. **65**, 1920 (1996).

[3] Y. Kobayashi, K. Fukui, T. Enoki, and K. Kusakabe, Phys. Rev. B **73**, 125415 (2006).

[4] Y. Niimi, T. Matsui, H. Kambara, K. Tagami, M. Tsukada, and H. Fukuyama, Phys. Rev. B **73**, 085421 (2006).

[5] J. Cai et al., Nature **466**, 470 (2010).

[6] K. Harigaya, H. Imamura, K. Wakabayashi, and O. Ozsoy, Journal of Superconductivity and Novel Magnetism, (to be published); http://arxiv.org/abs/1102.5473.

[7] M. P. Lima, A. J. R. da Silva, and A. Fazzio, Phys. Rev. B **81**, 045430 (2010).

[8] O. Özsoy, J. Optoelectron. Adv. Mater. **9**, 2283 (2007).

[9] O. Özsoy and K. Harigaya, J. Comput. Theor. Nanosci, **8**, 31 (2011).

[10] K. Harigaya, Jpn. J. Appl. Phys. **45**, 7237 (2006).

[11] T. Yoshioka, H. Suzuura, and T. Ando, J. Phys. Soc. Jpn. **72**, 2656 (2003).